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<p>(21) International Application Number: PCT/US00/11250</p> <p>(22) International Filing Date: 27 April 2000 (27.04.00)</p> <p>(30) Priority Data: 09/300,567 27 April 1999 (27.04.99) US</p> <p>(71) Applicant: CONDEA VISTA COMPANY [US/US]; 900 Threadneedle, Houston, TX 77079 (US).</p> <p>(72) Inventors: WEERASOORIYA, Upali; 11103 Andenwood Drive, Austin, TX 78726 (US). LIN, John; 4340 Auburn #C4, Lake Charles, LA 70607 (US). FILLER, Paul, A.; 201 County Road 180, Leander, TX 78641 (US). GATES, Frank; Box 3, McNeil, TX 78651-0003 (US).</p> <p>(74) Agent: BUSHMAN, C., James; Browning Bushman, Suite 1800, 5718 Westheimer Road, Houston, TX 77057 (US).</p>		<p>(81) Designated States: AU, BR, CA, IN, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: PROCESS FOR PREPARING AND ISOLATING SULFONATED INTERNAL OLEFINS</p> <p>(57) Abstract</p> <p>A product for producing and recovering sulfonated internal olefins wherein an internal olefin is sulfonated to produce a reaction mixture containing intermediate sulfonated compounds, the reaction mixture is neutralized and hydrolyzed to form a product mixture containing hydroxyalkane sulfonates, alkene sulfonates, and hydrocarbon oil, and the product mixture is subjected to azeotropic distillation to effect separation of the hydrocarbon oil from the product mixture.</p>		

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## PROCESS FOR PREPARING AND ISOLATING SULFONATED INTERNAL OLEFINS

### Cross-reference to Related Patents

This applications is related to U.S. Patent No. 5,488,148, entitled *Process for Sulfonating Internal Olefins*, issued January 30, 1996.

### Background of the Invention

#### 5 Field of the Invention

The present invention relates to a process for producing sulfonated internal olefins and, more particularly, to a process for isolating the internal olefin sulfonates from the reaction mixture.

#### Description of the Prior Art

- 10 Internal olefin sulfonates have utility as anionic surfactants that are widely used. Procedures for the sulfonation of internal olefins are well known and documented in the prior art. Procedures for sulfonating internal olefins are disclosed, for example, in the following references: European Patent Application No. 0446971A 1; Cavali, et al., *Comun. Jorn. Com. Esp. Deterg.*, 23, 1992, pp. 205-218; and Roberts, et al., *Comun.*
- 15 *Jorn. Com. Esp. Deterg.*, 22, 1991, pp. 21-35. European Patent Application No. 0446971 discloses that internal olefins having from 8 to 26 carbon atoms can be sulfonated in a falling film reactor with a sulfonating agent in a mol ratio of sulfonating agent to internal olefin of 1:1 to 1.25:1 while cooling the reactor with a cooling means having a temperature not exceeding 35°C and then neutralizing and hydrolyzing the reaction
- 20 product from the sulfonating step. The sulfonation of the internal olefins is preferably carried out with sulfur trioxide. The cooling means is preferably water having a temperature not exceeding 35°C, more preferably in the range of from about 0 to 25°C. The sulfonation may be carried out batchwise, semi-continuously, or continuously. The reaction is preferably performed in the falling film reactor, which is cooled by flowing
- 25 the cooling water at the outside wall of the reactor. At the inner walls of the reactor, the internal olefin flows in a downward direction, as does SO<sub>3</sub>. SO<sub>3</sub> is diluted with nitrogen, air, or any other gas, inert under the reaction conditions.

The Cavalli et al. reference teaches that internal olefins can be sulfonated by reacting the olefin and  $\text{SO}_3$ , aging, neutralizing the product with sodium hydroxide, and then hydrolyzing. Specifically, the Cavalli reference discloses that sulfonation can occur with an  $\text{SO}_3$ /olefin mol ratio of 1.025, an  $\text{SO}_3$ /air, 2.5%, an olefin flow rate of 14.5 kh/g, and a cooling jacket temperature of 8-10°C. As per the Cavalli reference, neutralization can be conducted with a 28% sodium hydroxide flow rate of 70 kg/h, a temperature of 30°C, and an average residence time of 30 min. Hydrolysis can be conducted at a temperature of 160°C and an average residence time of 40 minutes.

Roberts et al. disclose that internal olefins can be sulfonated in a tubular reactor using  $\text{SO}_3$  diluted so as to have a concentration of 2.5% in air, the reactor being cooled to between 10 and 32°C. In the sulfonation procedure, the olefin flow rate is 16.45 kh/g, and the  $\text{SO}_3$ /olefin mol ratio is 1.05. One of the clear advantages of the process of the present invention is that conventional batch-type reactors, requiring no special design, can be employed in sulfonating the internal olefins. Prior art workers employing neat internal olefins have generally had to employ falling film reactors or, in any event, specially designed reactors in order to obtain a product of good quality and in high yields. Problems as to specially designed reactors are obviated by the process of the present invention.

Recently, internal olefins have been sulfonated under conditions to produce products that are rich in hydroxyalkane sulfonates with low levels of residual sultones, inorganic sulfates, and free oil. In an article by J. Stapersma, H. H. Deuling, and R. Van Ginkel entitled "Hydroxy Alkane Sulfonate (HAS), a New Surfactant Based on Olefins," *JAOCS*, Vol. 69, No. 1, January 1992, pp. 39-43, there is described the production of hydroxyalkane sulfonates from internal olefins using a falling film glass reactor under mild conditions. Using this technique, it is possible to obtain a product that is rich in hydroxyalkane sulfonates.

In U.S. Patent No. 5,488,148, incorporated herein by reference for all purposes, there is disclosed a process for sulfonating internal olefins wherein internal olefins present in an amount of from about 5 to about 40% by weight in a substantially inert hydrocarbon solvent are sulfonated under well-known sulfonation conditions to produce intermediate sulfonated compounds that are then neutralized and hydrolyzed to form a product mixture containing HAS and alkene sulfonates, the product mixture being

recovered. The process disclosed in U.S. Patent No. 5,488,148 also teaches that the desired, internal olefin sulfonates are extracted into an aqueous phase using an alcohol such as isopropanol, the aqueous phase subsequently being backwashed with an inert hydrocarbon such as hexane to remove any remaining paraffin. Since the isopropanol and some residual hexane remain in the aqueous phase, it is necessary to recover the internal olefin sulfonates by volatilizing the water, the alcohol, and the hexane.

### Summary of the Invention

It is therefore an object of the present invention to provide a process for producing and recovering sulfonated internal olefins.

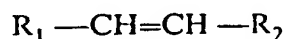
Another object of the present invention is to provide a process for isolating sulfonated internal olefins obtained either from neat olefin sulfonation or sulfonation of internal olefins in a hydrocarbon solvent.

Yet a further object of the present invention is to provide a process for isolating internal olefin sulfonates that reduces the number of processing vessels needed and obviates the need for removal and recycle of volatiles.

Still another object of the present invention is to provide a process for recovering internal olefin sulfonates produced by the sulfonation of neat internal olefins wherein the amount of free oil present in the internal olefin sulfonates is significantly reduced.

The above and other objects of the present invention will become apparent from the description given herein and the appended claims.

According to the process of the present invention, an internal olefin having the general formula:



, wherein  $R_1$  and  $R_2$  may be the same or different and are each an alkyl group containing from about 1 to about 30 carbon atoms, is sulfonated with a suitable sulfonating agent to produce a reaction mixture containing intermediate sulfonated compounds. The intermediate sulfonated compounds in the reaction mixture are neutralized and hydrolyzed to form a product mixture containing hydroxyalkane sulfonates, alkene sulfonates, and hydrocarbon oil. The product mixture is subjected to azeotropic

distillation with water to effect separation of the hydrocarbon oil from the product mixture.

### Description of the Preferred Embodiments

In the process of the present invention, the internal olefins, neat or in the form of a dilute solution in a hydrocarbon solvent, are sulfonated in a suitable vessel using vaporized sulfur trioxide in a carrier stream, generally heated air, that is passed through the internal olefin starting material. Generally speaking, the sulfur trioxide is introduced so as to provide a mol ratio of sulfur trioxide to internal olefin of from about 1.0:1.0 to about 3.0:1.0. In general, the sulfonation temperature is maintained in the range of from about the freezing point of the inert olefin starting material to about 30°C, preferably to about 10°C.

The sulfonation reaction produces a reaction mixture containing intermediate sulfonated compounds that are neutralized, generally in the same temperature range discussed above before the sulfonation reaction, with a basic material, such as an aqueous solution of an alkali metal hydroxide, ammonium hydroxide or alkanolamine, or another commonly used neutralizing agent. Preferably, the neutralization is carried out using an aqueous alkali metal hydroxide solution, such as a sodium hydroxide solution.

To effect hydrolysis of the sultones, the neutralized reaction mixture can be refluxed at a temperature of from about 100°C up to about 160°C for a period of time sufficient to convert the sultones either to the hydroxyalkane sulfonates or the alkene sulfonates. Alternatively, hydrolysis can be accomplished by placing the neutralized reaction mixture into a pressurized stainless steel vessel and subjected to heating at a temperature of from about 100°C to about 160°C for a period of time sufficient to convert the sultones to the hydroxyalkane sulfonates or the alkene sulfonates, care being taken to maintain the neutralized reaction mixture being hydrolyzed at a pH of about 11 or greater.

The hydrolysis step produces a product mixture containing hydroxyalkane sulfonates, alkene sulfonates, and hydrocarbon oil (free oil). This product mixture is then subjected to azeotropic distillation using water. This can be conveniently carried out in a magnetically stirred, heated stainless steel vessel, the internal temperature of the vessel being monitored by a suitable controller, which injects air through a cooling coil as

needed. Provision is made to inject water into the vessel and permit the escape of steam. Generally, the azeotropic distillation is conducted at a temperature of from 100 to 160°C at a pressure of from about 15 to about 80 psig. The water-oil azeotrope is condensed and measured, a volume of water equal to that in the recovered azeotrope being introduced into the vessel. This approach essentially maintains the volume of the mixture in the reactor constant during the azeotropic step.

To more fully illustrate the present invention, the following non-limiting examples are presented.

Example 1: Sulfonation of Neat Internal Olefins

10        An internal olefin blend marketed by CONDEA Augusta and comprised of C<sub>15</sub>-C<sub>16</sub> internal olefins (90.62%), C<sub>15</sub>-C<sub>16</sub> paraffins (3.42%), and C<sub>15</sub>-C<sub>16</sub> aromatics (5.96%) was used as the sulfonation feedstock. The reaction system consisted of a syringe pump, a glass, sulfur trioxide vaporization chamber, a glass sulfuric acid trap, and a glass tubular sulfonation reactor containing a perforated glass disk base for the bubbling of the

15        air-sulfur trioxide mixture through the sulfonation feedstock. A side arm of the reactor supported a thermometer that was kept in contact with the feedstock. The vaporization chamber and acid trap contained thermocouples and were wrapped with heating tape connected to Variacs for temperature control. Liquid sulfur trioxide was measured into a gas-tight syringe equipped with a long needle for transfer to the top of the vaporizer

20        from the syringe pump. The liquid sulfur trioxide is injected so as to run down the inside wall of the vaporizer. In the vaporization chamber, sulfur trioxide is vaporized to form an air-sulfur trioxide blend, which is then passed through another glass vessel set at a slightly lower temperature to entrain sulfuric acid droplets. The air-sulfur trioxide blend then passes through the sulfonation feedstock in the sulfonation reactor and escapes from

25        the reactor via a vent. In this example, 50 g (212 mmol) of C<sub>15-16</sub> internal olefins containing 3.42 weight % paraffin (aliphatic hydrocarbons) and 5.96 weight % aromatics was poured into the 150 ml capacity sulfonation reactor with an air flow rate of 10-11 l/min. Sulfur trioxide, 12.9 ml (318 mmol), was injected into the vaporizer at a rate of 0.5 ml/min. The vaporizer was kept at 290°F. The acid trap was maintained at 270°F.

30        The sulfonation reaction temperature was maintained at about 25°C using a water-ice bath as needed through the reaction. The reaction mixture progressively thickened and

darkened as more sulfur trioxide was added. Immediately after cessation of sulfur trioxide addition, the reaction mixture was decanted with efficient stirring into a beaker containing a chilled solution of 50.9 g (636 mmol) of 50 weight % aqueous sodium hydroxide and 25 ml of water. An additional 50 ml of water was used to rinse the sulfonation reactor. The contents of the beaker were mechanically stirred at room temperature for approximately 40 min. to effect partial hydrolysis of the sultone intermediates. The pH remained above 11 throughout. To neutralize the residual sultones, the reaction mixture was transferred into a closed stainless steel bomb and heated at 160°C for 50 minutes. During this time, the pressure reached approximately 77 psig. The final pH of the hydrolyzed, product mixture was found to be above 11. Upon cooling to ambient temperature, concentrated sulfuric acid was carefully added with good mixing to adjust the pH to about 8. At this point, the product mixture, which contained hydroxyalkane sulfonates, alkene sulfonates, hydrocarbon oil, sodium sulfate, and water, was a dark brown gel.

Recovery of Sulfonated Internal Olefins and Free Oil Removal. The product mixture was introduced into a stainless steel bomb having a capacity of about 400 ml. The bomb was heated by placing it in a block controlled by a Therm-O-Watch. The internal temperature of the bomb was monitored by a controller that injected air through a cooling coil as needed. Water was introduced from a stainless steel, pressurized reservoir (equipped with a glass side arm) via a dip tube built into the bomb cap. Steam escaped through a needle valve vent connected by tubing to a Claisen head mounted on a graduated cylinder and topped with a chilled condenser set at -2°C. As the neutralized reaction mixture was stirred in the closed bomb, heating was applied to reach a final temperature of 160°C. A bleed of steam was created by carefully and partially opening the vent. The pressure inside the bomb dropped from about 80 to about 50 psig. Care was taken to control the bleed so as to avoid the escape of foam. The water-oil azeotrope was condensed and measured in the graduated cylinder. Fresh water was forced into the reactor using a head pressure of about 80 psig. In this manner, an equal volume of water was introduced for the volume distilled and condensed in the graduated cylinder. Typically, the water was introduced in 15 ml portions. This approach prevented any excessive change of the volume of the contents in the reactor during the azeotroping step. Over a period of 1.5 hours, a total of 122 ml of distillate was collected. The expected



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amount of free oil, about 2 ml, was observed. No oil layer appeared in the newly condensed distillate. At ambient temperature, the final sample was a muddy tan to brown slurry found to contain 28.4 weight % active internal olefin sulfonate and 0.88 weight % free oil. This translate to 3 weight % free oil based on active internal olefin sulfonate.

- 5 By way of comparison, neutralized reaction mixture before azcotrope contained 27.6 weight % sulfonated internal olefin and 1.54 weight % free oil. This translate to 5.3 weight % free oil based on active.

This example clearly demonstrates that by using the process of the present invention, neat internal olefins can be sulfonated to produce sulfonated internal olefins  
10 containing a minimum amount of free oil. It also demonstrates that one does not need to force sulfonation of the internal olefins to completion because the unreacted olefins can be reduced as part of the free oil.

#### Example 2

- A sulfonation feedstock comprised of 13 weight % internal olefins in a C<sub>14-16</sub>  
15 paraffin solvent was prepared. The sulfonation apparatus utilized for sulfonating the dilute mixture of internal olefins was substantially that as described above in Example 1, with the exception that a larger glass sulfonation reactor was employed to accommodate the higher volume of sulfonation feedstock. Additionally, because foaming in the dilute solution poses a problem at the beginning of the reaction, the air  
20 flow rate was initially set low and gradually raised to the desired level. A 500 g (311 mmol) aliquot of the sulfonation feedstock was charged into a 1-liter glass sulfonation reactor with the air flow set at approximately 3l/min. Sulfur trioxide, 19.0 ml (468 mmol), was injected into the vaporizer at 0.5 ml/min. The vaporizer was set at a temperature of 290°F. The acid trap was maintained at 270°F. The air flow could be  
25 gradually increased as sulfur trioxide reacted. The final, desired flow rate was achieved when 1 ml of sulfur trioxide had been introduced into the reaction mixture. The reaction mixture was kept at 25°C through the sulfur trioxide injection. Following completion of sulfur trioxide addition, the reaction mixture was decanted with efficient stirring into a beaker containing a chilled solution of 74.6 g (933 mmol) of 50 weight % aqueous  
30 sodium hydroxide and 200 ml of water. Another 200 ml of water was used to rinse the tar from the sulfonation reactor into the beaker. The neutralized mixture, which was a

slurry, was mechanically stirred at room temperature for approximately 40 minutes. The pH remained above 11 throughout. The neutralized mixture was subjected to hydrolysis in a closed 400 ml stainless steel bomb at 160°C for 50 minutes. The maximum pressure observed was about 80 psig. Because of the larger volume, this step was accomplished in four batches. Care was exercised to mix the slurry well before dividing into the four batches. The pH of the hydrolyzed, product mixture containing hydroxyalkane sulfonates, alkene sulfonates, and hydrocarbon oil was found to be above 11 without the addition of more base. The four batches were then recombined for neutralization. At ambient temperature, concentrated sulfuric acid was carefully added to adjust the pH to between 7 and 8 to form a yellow emulsion.

Recovery of Sulfonated Internal Olefins and Free Oil Removal. Approximately one-fourth of the product mixture from the hydrolysis step was transferred into the reactor described above in Example 1 with respect to free oil removal. The azeotrope was conducted at 160°C and about 80 psig. Approximately 1.7 l of water was passed through the reactor and collected over a period of 9 hours before the distillate no longer showed a separate, paraffin layer. The volume in the reactor was further reduced by 350 ml before cooling to ambient for introduction of a second one-fourth portion of the product mixture. Azeotropic removal of oil from the second portion also required 9 hours and about 1.7 l of water. The final, approximately 276 g, of product mixture was dark brown to burgundy and clear with no visual signs of an oil layer. The slurry was found to contain 15.8 weight % active and 0.2 weight % free oil, which translates to 1.7 weight % free oil based on active internal olefin sulfonate.

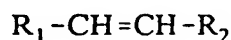
This example demonstrates that using the process of the present invention, dilute feedstocks of internal olefin sulfonates can be effectively sulfonated to produce an internal olefin sulfonate product containing very low amounts of free oil. It also demonstrates that one does not have to force the sulfonation reaction to completion to achieve a product low in free oil.

The foregoing description and examples illustrate selected embodiments of the present invention. In light thereof, variations and modifications will be suggested to one skilled in the art, all of which are in the spirit and purview of this invention.

**What is claimed is:**

1. A process for producing and recovering sulfonated internal olefins comprising:

sulfonating internal olefins having the general formula:



wherein  $R_1$  and  $R_2$  may be the same or different and are each an alkyl group containing from about 1 to about 30 carbon atoms with a sulfonating agent to produce a reaction mixture containing intermediate sulfonated compounds;

neutralizing and hydrolyzing said intermediate sulfonated compounds in said reaction mixture under conditions to form a product mixture containing hydroxyalkane sulfonates, alkene sulfonates, and hydrocarbon oil; and

subjecting said product mixture to azeotropic distillation to effect separation of said hydrocarbon oil from said product mixture.

2. The process of Claim 1 wherein said internal olefins are present in a hydrocarbon solvent that is substantially inert under sulfonation conditions and does not deleteriously affect sulfonation of said internal olefins, said internal olefins being present in said hydrocarbon solution in an amount of from about 8 to about 20% by weight.

3. The process of Claim 1 wherein said sulfonation is conducted using gaseous sulfur trioxide as a sulfonating agent.

4. The process of Claim 1 wherein said neutralization is conducted using an alkali metal hydroxide solution.

5. The process of Claim 2 wherein said hydrocarbon solution comprises a mixture of paraffinic hydrocarbons.

6. The process of Claim 1 wherein  $R_1$  and  $R_2$  are alkyl groups, each one of  $R_1$  and  $R_2$  containing from about 4 to about 15 carbon atoms.

7. The process of Claim 1 wherein said azeotroping is conducted at a temperature of from about 100 to about 170°C.

8. The process of Claim 1 wherein said azeotroping is conducted at a pressure of from about 15 to about 80 psig.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/11250

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C07C 309.00

US CL : 562/115 ; 562/123

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 562/115 ; 562/123

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

search terms: paraffin, azeotropic, internal olefin, sulfonating

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,488,148 A (WEERASOORIYA et al) 30 January 1996 (30.01.96), col. 2, lines 1-2, 20-38, 46-48, 50-56, and 63-64.	1-6
Y	US 3,887,611 A (SWEENEY et al) 03 June 1975 (03.06.75), col. 1, lines 14-15; col. 2, lines 10-13; col. 4, lines 25-41.	1, 7-8



Further documents are listed in the continuation of Box C.



See patent family annex.

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